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Introduction

The recent discoveries of nonmolecular phases of simple molecular solids [1,2] demonstrate the proof-of-the-principles for producing exotic phases by application of high pressure. Modern advances in theoretical and computational methodologies now make possible to explain or even predict novel structures and properties in a relatively wide range of length scales on the basis of thermodynamic stability [3]. Equally important in materials research is the recent developments in advanced x-ray and laser diagnostics that enable in-situ observations at the formidable pressure-temperature conditions [4]. Having benefited by all these developments, we discuss the first principle of the pressure-induced chemistry, "*Mbar Chemistry*", with a few examples that may have important implications in materials research.

Mbar chemistry

At 100 GPa, localized electrons develop huge kinetic energy and, thereby, can strongly mix with valence and core electrons of its own or nearby molecules. Such a core swelling and/or a valence mixing create an excellent environment for simple molecules to chemically transform into nonmolecular extended solids such as polymeric and metallic solids. At these pressures, the compression energy (PΔV) of molecular solid often exceeds an eV or 100 KJ/mol, rivaling those of the most stable chemical bonds and certainly enough to induce chemistry acquiring bond scissions. The products are controlled by collective behaviors of molecules, leading to strongly associated phases in a pressure range of 10-50 GPa [5], multi-dimensional polymeric products at around 50 and 100 GPa [6], and eventually band-gap closing molecular and atomic metals typically above 100 GPa [7] (Fig.1). At sufficiently high pressures of ~1 TPa, most solids will lose their periodic integrities and the system with simple or no core electrons (*e.g.* H_2 and He) may even convert into a bare nuclei.

The materials at high temperatures, on the other hand, often transform into an open structure like bcc because of a large increase of entropy. Further increasing temperatures well above the melt will eventually ionize, dissociate or even decompose molecules into elemental atoms. Such a temperature-induced ionization would eventually produce a conducting state of matter if the pressure were sufficiently high. Therefore, the combined effect of high pressure and high temperature will provide a way of probing a delicate balance between mechanical (PΔV) and thermal (TΔS) energies or between pressure-induced electron delocalization and temperature-induced electron ionization, reflected on stabilities of phases and the phase boundaries. These pressure-temperature induced changes are unique, establishing an entirely different set of periodic behaviors in crystal structure and electronic and magnetic properties unfound in the conventional periodic table. In return, this is what makes the "*Mbar chemistry*" unique from any ambient-pressure combinatorial chemistry based on variation of chemical composition and temperature. New opportunities to discover interesting phenomena and exotic materials exist in both liquids and solids at high pressures.

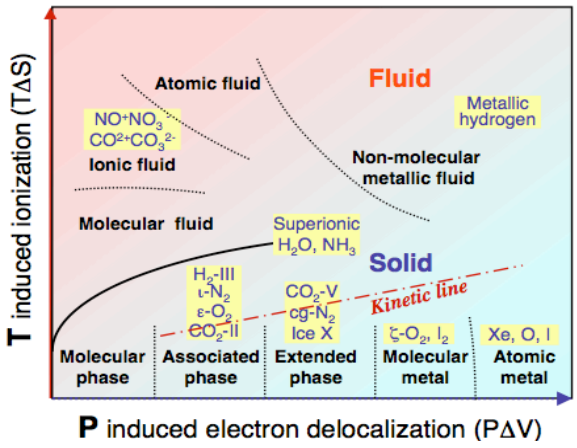

Figure 1. *Conceptual chemical phase diagram of low-Z molecular solids to illustrate their structural modification at high P-T conditions. Overlaid are nonmolecular phases of simple low-Z molecules previously observed in high-pressure experiments and theoretical studies.*

The development or realization of these predicted, potentially useful materials is, however, controlled by the stability as well as the metastablility of solids. The existence of intermediates, such as a strongly associated phase in Fig. 1, could substantially lower the transition threshold for forming an extended solid. Furthermore, these materials are balanced by an entirely new set of interactions, strong chemical bonds and dipole interactions, replacing mostly weak quadruples in molecular solids. As a result, these materials greatly enhance the strength, sustaining large lattice distortions and strains and resulting in its metastability (*i.e.*, a large activation barrier toward the backward transformation). In fact, many nanoparticles and surface structures are engineered based on knowledge of their metastability. Thereforere, it is important in materials reearch to understand the exact nature of phase dynamics and kinetics associated with the phase transitions.

High pressure experiments

Recent advances in diamond-anvil cell (DAC) high-pressure technologies coupled with micro probing laser and advanced third-generation synchrotron x-ray offer unprecedented opportunities to discover novel phases of materials at high pressure-temperature conditions of Earth and other Giant planetary interiors [8]. Single-crystal and powder

diffraction using hard x-rays (energies above 10 keV) offer the most definitive information on crystal structure and atomic packing, and is complemented by laser Raman and synchrotron inelastic x-ray Raman spectroscopies [9] that probe molecular vibrations and near-neighbor interatomic bonding, respectively. Furthermore, recent developments of the beamlines dedicated to high-pressure science at third-generation sources offer greatly enhanced if not revolutionary opportunities for high-pressure materials research.

While DAC is capable of generating high pressures to several 100 GPa, the precise and tunable control of de/compression rates has been a formidable challenge to high-pressure materials research. Such a limitation has hindered studies of transition dynamics along pressure-induced phase transformation paths and materials metastability. To remedy this situation, we have recently developed a new enabling technique dynamic-DAC (dDAC), capable of fine controls of pressures and (de)compression rates [10]. Coupling with time-resolved synchrotron x-ray and laser spectroscopic methods, dDAC enable us to study time-resolved structural evolution and structure-stress-functional relationship of the sample in DAC. Clearly, those information obtained by dDAC experiments is critical to gain insight of metastability and local energy minimum configuration- beyond stable phases with minimum energy configurations.

Results and Discussion

In this paper, I will discuss recent results of high-pressure chemistry/physics arising from pressure-induced electron delocalization in simple low-z molecular solids at pressures of 100 GPa, following the brief descriptions of modern DAC technololgies coupled with laser-heating and synchrotron x-ray diffraction and spectroscopy. Several examples of high-pressure materials research utilizing third-generation synchrotron x-ray technologies will be given among simple C-O-H-N compounds. Also presented are future directions of high-pressure synchrotron materials research using dynamic-DAC in an emerging/complementary phase and time scales of shock and static high pressures.

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